A comparative study on different metal loaded soybean milk by-product 'okara' for biosorption of phosphorus from aquaeous solution

T.A.H. Nguyen [a], H.H. Ngo [a*], W.S. Guo [a], T.V. Nguyen [a], J. Zhang [b], S. Liang [b],
S.H. Chen [c], N.C. Nguyen [c],

[a] *Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology, Sydney, Broadway, NSW 2007, Australia*

[b] *Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science & Engineering, Shandong University, Jinan 250100, PR China*

[c] *Institute of Environmental Engineering and Management, National Taipei University of Technology, No.1, Sec. 3, Chung –Hsiao E. Rd, Taipei 106, Taiwan, ROC*

* Corresponding author: School of Civil and Environmental Engineering, University of Technology, Sydney (UTS), P.O. Box 123, Broadway, NSW 2007, Australia. Tel.: +61 2 9514 2745; Fax: +61 2 9514 2633. *E–mail address:* ngohuuhao121@gmail.com

ABSTRACT

Cationization of agricultural by-products using metal salts is widely used to activate their phosphorous capture ability. This study developed three kinds ofnew metal loaded soybean milk by-product 'okara' for phosphorus biosorption. A comparative study among these biosorbents was carried out with respect to their performances in terms of affinity, stability and reusability. Zirconium loaded okara (ZLO) was found to have the highest affinity towards PO_4^{3-} anions (47.88 mg/g), followed by iron/zirconium loaded okara – IZLO (40.96 mg/g) and iron loaded okara – ILO (16.39 mg/g). ZLO was successfully desorbed with 0.2 M NaOH and activated with 0.1 HCl prior to the next cycle. After five consecutive cycles, the efficiency of both adsorption and desorption of ZLO remained about 85% whilst no Zr(IV) leakage was observed. Conversely, IZLO and ILO suffered from vitalshortcomingssuch ashigh metal release and/or sharp reduction in PO_4^{3-} sequestering capability after multi operation cycles.

Keywords: Metal loaded okara; Phosphorus removal; Biosorption; Desorption; Reusability

1. Introduction

Phosphorus is known as an essential element to the plant growth (Ismail, 2009). It is also a key constituent of deoxyribonucleic acid (DNA), teeth and bones in animal bodies (Biswas, 2008). Moreover, it is a fundamental material for many industries, including fertilizers, detergents, pharmaceuticals, beverages, paints and corrosion inhibitors (Biswas et al., 2007). Nevertheless, due to the overexploitation for different uses, the global rock phosphorus reserves are at the risk of being exhausted in 50−100 years (Eljamal et al., 2013; Ogata et al., 2012). Thus, there is an urgent need to search for alternative sources of phosphorus (Anirudhan et al., 2006; Zhang et al., 2012).

In another perspective, phosphorus is considered as a pollutant that causeseutrophication with the concentration in receiving water of higher than 0.02 mg/L (Jyothi et al., 2012; Mallampati and Valiyaveetttil, 2013). To protect aquatic medium from eutrophication, in many countries,phosphorus level is regulated to be lower than 0.05 mg/L, if streams discharge into lakes or reservoirs (Benyoucef and Amrani, 2011). As a result, the elimination of phosphorus from effluents before discharging is mandatory (Kalmykova and Fedje, 2013).In addition, the removal of phosphorus enables its recovery for the substitution of depleting phosphorus ores.

So far, numerous available technologiesfor controlling PO_4^{3-} pollution can be grouped into chemical, biological and physical methods (Benyoucef and Amrani, 2011; Bhojappa, 2009).Though chemical precipitation and biological processes are most commonly used, adsorption has attracted an increasing attention, with dominant advantages of being effective, best suited for low levels of PO_4^{3-}, and favorable to PO_4^{3-} recovery (Li et al., 2009; Loganathan et al., 2013; Zhang et al., 2011). Due to drawbacks of commercial adsorbents (e.g. high cost, non−renewability), there is lately an emerging trend to use agricultural wastes/byproducts (AWBs) based biosorbents for this purpose.

Due to the lack of anion binding sites on their surface, most of AWBs in the natural form are inefficient in removingPO_4^{3-} from aqueous solutions (Eberhardt and Min, 2008). Thus, to augment their affinity toward PO_4^{3-}, AWBs need to be cationized, which can be implemented via metal loading, hybridizing with inorganic chemicals, and grafting with ammonium type chemicals (Han et al., 2005; Mallampati and Valiyaveettil, 2013).Metal loading is usually a method of choice because of its simplicity and efficiency. Although much research has been done on the removal of PO_4^{3-} using metal loaded AWBs based biosorbents, their practical application is still limited. This can be attributed to the fact that the stability and reusability of biosorbents have usually received far less attention than their adsorption and desorption capacities.

Okara is one of the well-known agricultural by-products, which is collected from production of soymilk, tofu and their derivatives. It can have different names, such as soybean milk residue, soy pulp, soy fines, bean mash, bean curd dreg (English), le okara (French), das okara (German), tofuzha, douzha or doufuzha (Chinese), tofukasu (Japanese), piji(Korean),sapal(Filipino), ampastahu (Indonesian), tauhu tor (Thai). The production of every 1,000 L of soy beverage can result in 250 kg of okara (Soy 20/20). Based on the soy beverage consumption, it is estimated that around 14 million tons of okara are annually generated worldwide. As okara contains 50% fiber, 25% protein, 10% lipid, and other nutrients, it is desirable to use okara as animal feed, fermentation substrate, fertilizer, pet food, food production, etc. However, the rapid degradation, high cost of drying, feasibility of freezing, etc. are major barriers to the use of okara in food. Currently, okara is mostly dumped or burned as waste, except for a small quantity, which is occasionally used as animal feed (Li et al., 2012). This can pose a risk to the environment. Consequently, there is a need to develop useful products from this waste material. Some types of soybean by-products were used as environmentally friendly materials in water treatment, such as soybean hulls (Marshall and Wartelle, 2004); lees materials (Adachi et al., 2005); bean dregs (Li, 2009); and okara (Gao et al., 2011). It was found that these materials exhibit diverse sorption capabilities toward anions (i.g.AsO_4^{3-}, CrO_4^{2-}, $Cr_2O_7^{2-}$, PO_4^{3-}, SeO_4^{2-}); organochlorine compounds or benzen; heavy metals (Cu^{2+}, Zn^{2+}); dyes (acid red 14 and reactive red 15), respectively. However, to the best of the authors' knowledge, no previous studies have reported the application of okara for phosphate pollution remediation.

Okara was chosen for investigation in this study because of its insolubility in water, non-toxicity, low cost, easy acquiring, and abundant availability. Moreover, the present research found that okara has about 200-250 mg P/ 100 g dry okara phosphorous inside itself (200-250 mg P/ 100 g dry okara). This can provide a foundation for the recovery of phosphorus from both original okara and wastewater. Due to the poor ability of pristine okara in eliminating phosphorus from aqueous solution, modified okara was prepared and utilized for this purpose. The 7previous study with iron load okara (ILO) demonstrated an unsatisfying adsorption capacity (4.785 mg PO_4/g), and thevigorous detachment of Fe(III) during operation (Nguyen et al., 2013).Hence, the objective of this work is to develop new kinds of metal loaded okara, which hold enhanced adsorption capacity and superior stability. Particularly, for the very first time, the recyclability of new biosorbents was investigated. This paper reportedresults from adsorption experiments, desorption studies, stability and reusability investigations.Based on the obtained results, the best suitable metal loaded okara was recommended.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were of analytical grade.

The stock solution of phosphorus (1000 mg/L) was prepared by dissolving4.58 g of disodium hydrogen phosphate (Na_2HPO_4) in a 1000 ml of milli-Q water. The working solutions of phosphorus (10, 25, 50, 100, 125, 200, 250, 400, 500mg P/L) were prepared by diluting the stock solution (1000 mg P/L) with milli-Q water accordingly (100, 40, 20, 10, 8, 5, 4, 2.5, 2 times).

0.05 M and 0.2 M NaOH solutions: 2 and 8 g of sodium hydroxide (NaOH), respectively were dissolved in 1000 ml of milli-Q water.

0.25 M Fe(III) solution:40.55 g of ferric chloride ($FeCl_3$) was dissolved in 1000 ml of milli-Q water.

0.25 M Zr(IV) solution: 80.56 g of zirconyl chloride octahydrate ($ZrOCl_2.8H_2O$) was dissolved in 1000 ml of milli-Q water.

2.2. Preparation of metal loaded okara

Fresh okara was obtained from soybean milk production at home with Lumina glass blender (Model No BL–805C). 1 kg of okara was obtained from 4 liters of soybean milk. Prior to chemical modifications, fresh okara was washed on a sieve of 300 µm with tap water, and then with distilled water to remove the residual milk. It was then dried in the oven at 105 ^{0}C for 24 h,and kept in a desiccator prior to further treatment.

To prepare single metal loaded okara (ILO and ZLO),the dried raw okara was first stirred with 0.05 M NaOH at the following conditions: solid/liquid ratio of 1 g/20 ml, stirring speed of 120 rpm, room temperature, and contact time of 24 h. Secondly, NaOH treated okara was washed with tap water,and then with distilled water until pH of the washing solution was almost neutral. Next, it was dried in the oven at 105 ^{0}C for 24 h andcooled down to the ambient condition. Dried NaOH treated okara was then stirred with 0.25 M Fe(III) or 0.25 M Zr(IV) at the above condition. After washing with tap water and then with distilled water to remove all free metal ions on the surface, the materials weredried in the oven at 105 ^{0}C for 24 h and cooled down to the room temperature.

To prepare combined metal loaded okara (IZLO),the dried raw okara was pretreated with 0.05 M NaOH and then loaded with 0.25 M $FeCl_3$ as mentioned above. Next, the dried NaOH/$FeCl_3$ treated okara was stirred with 0.25 M Zr(IV) at the same conditions as mentioned above. After washing carefully with tap and then with distilled water to remove free Zr(IV) ions, the material was dried in the oven at 105 ^{0}C for 24 h and cooled down to the room temperature.

2.3. Experimental set–up

The experimental set-up in this study is shown in Fig. 1 and described in detail as the follows:

Figure 1

2.3.1. Adsorption studies

The adsorption experiments were carried out with okara in the modified forms, as follows:0.5 g of each metal loaded okara was taken into 9 conical flasks of 250 mL containing 50 ml of different phosphorus solutions (10, 25, 50, 100, 125, 200, 250, 400, 500 mg P/L). The pH of the solutionswas kept natural. The samples were shaken at the speed of 120 rpm, room temperature, for 24 h to ensure the equilibrium could befully reached. After the equilibrium time, the samples were filtered with Whatman™ 1822–047 Grade GF/C filter paper (diameter: 4.7 cm, pore size: 1.2 µm). The filtrate was taken for phosphorus determination. The phosphorus adsorption capacity (mg/g) was calculated from the difference between initial and equilibrium phosphorus concentrations as follows:

$$q = \frac{(C_i - C_e) * V}{m} \qquad (1)$$

where, C_i and C_e are the initial and equilibrium phosphorus concentrations in the solution (mg/L), respectively; V is the volume of the solution (L); and m represents the dry weight of the metal loaded okara powder (g).

The adsorption equilibrium was investigated using Langmuir and Freudlich isotherms models.

2.3.2. Desorption and regeneration studies

After adsorption, the spent metal loaded okara (0.5 g) as separated from the solution by filtration with Whatman™ 1822–047 Grade GF/C filter paper (diameter: 4.7 cm, pore size: 1.2 µm). The phosphorus bearing metal loaded okara was washed lightly with tap and then with distilled water to eliminate unadsorbed phosphorus. The solid was then collected into 5 conical flasks of 250 mL, containing 50 ml of 5 elution solutions (i.g. 0.2 M NaOH, 0.05 M NaOH, pH 12 distilled water, 0.1 M NaCl, and 0.1 M HCl). All samples were agitated on an orbital shaker at the speed of 120 rpm, room temperature for 24 h. After that time, the solid was removed from the solution by filtration again. The filtrates were used to evaluate thedesorbed phosphorus amounts. Based on the desorption results, the potential eluant was identified and used for generation studies with both ZLO and IZLO.

After desorption with the potential eluant, the spent metal loaded okara were reused for other 4 continuous adsorption – desorption cycles, with or without activation by 100 mL of 0.1 M HCl. The P removal percentage was used to determine the reusability of these two biosorbents.

2.3.3. Identification of metal quantity deposited on okara

The process to estimate the metal amounts deposited on okara was adapted from Boujelben et al. (2008).In this study, thetreatmentled to the dissolution of metals deposited on okara in concentrated nitric acid (HNO_3).1 g of each biosorbent (i.g. ILO, IZLO, ZLO) was mixed at 50 ^{0}C with 10 mL of concentrated HNO_3 (70%, density 1.42 g/cm^3, molarity 15.8) and shook for 30 min, and then with 20 mL of 0.1 M $HNO_3$and shook for 1 h. After that, the suspension was filtered with Whatman™ 1822–047 Grade GF/C filter paper (diameter: 4.7 cm, pore size: 1.2 µm)for metal analysis.

2.3.4. Determination of metal leakage during adsorption and desorption tests

After adsorption and desorption, suspensions were filtered through Whatman™ 1822–047 Grade GF/C filter paper (diameter: 4.7 cm, pore size: 1.2 µm). The filtrates were used to identify the metal concentrations.

2.3.5. Determination of the content of phosphorus inside okara

To identify the content of phosphorus inside okara, the authors have prepared samples according to the procedures described by Vietnam standards TCVN 8551:2010, Plants – Method for sampling and preparing sample, which was issued on 29 December 2010, at the Decision of 2945/QĐ-BKHCN. The concentration of phosphorus in the obtained solution was then determined spectrophotometrically by molybdenum blue method on Spectroquant® NOVA 60.

2.3.6. Effect of co-anions on the removal of phosphorus by ZLO

The influence of typical foreign anions, such as sulfate (SO_4^{2-}), nitrate (NO_3^-), chloride (Cl^-) and carbonate (CO_3^{2-}) on the adsorption of phosphate (PO_4^{3-}) was investigated. The KCl, KNO_3, K_2CO_3 and Na_2SO_4 salts were used to prepare the corresponding foreign anion solutions. 1 g of ZLO was added into a flask containing 50 mL of phosphorus solution, which was mixed with one foreign anion separately or four foreign anions simultaneously. The molar concentration of each foreign anion in the combined solution was 10 fold higher than that of phosphorus. The experiment was performed at the initial phosphorus concentration of 100 mg P/L (~ 3 mmol PO_4/L), original pH, 25^0C, and agitation speed of 120 rpm for 24 h, in the presence of single or multi foreign anions. The control experiment was conducted at the same conditions, in the absence of foreign anions.

2.4. Analytical methods

2.4.1. Determination of phosphorus content in the solution

Phosphorus concentrations of the solutions before and after adsorption were determined spectrophotometrically using molybdenum blue method on Spectroquant® NOVA 60. Experiments were implemented in triplicate and the data represented the mean values. The highest acceptabledeviation was 5%.

2.4.2. Identification of metal concentration in the solution

The concentration of metals released into the solution during adsorption and desorption tests was measured using MicrowavePlasma–Atomic Emission Spectrometer (MP–AES) – Agilent Technologies 4100.

2.4.3. Physical characteristics of the chosen metal loaded okara (ZLO)

This study investigates such physical characteristics of ZLO as density, porosity, and permeability. The density and porosity of ZLO were determined using procedures outlined by Okochi (2013). The permeability coefficient of ZLO was determined using Darcy's Law (http://www.ajdesigner.com/phppermeameter/permeameter_equation_permeability_coefficient.php). The experiment design is illustrated in Fig. 2.

$$K = \frac{Q\Delta L}{A\Delta h} \tag{2}$$

where, K is the permeability coefficient (m/day) Q is the porous medium flow rate (m^3/s), ΔL is the length change (m), A is the cross sectional area (m^2), ΔH is the pressure head change (m).

Figure 2

3. Results anddiscussion

3.1. Adsorption isotherm

Equilibrium studiesare essential to determine the adsorption capacity of ZLO, IZLO and ILO. The initial phosphorus concentrationused in this study was in the rangeof 10–500 mg/L. The isotherm data was analyzed using two of the most widely used equilibrium models, Langmuir and Freundlich. The linear expressions of Langmuir and Freundlich isotherms are given as follows (Krishnan and Haridas, 2008):

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

where, q_e is the amount of phosphorus adsorbed per unit weight of biosorbent (mg/g), C_e is the equilibrium phosphorus concentration (mg/L), $q_m$and K_L are Langmuir constants, representing the maximum adsorption capacity (mg/g) of the biosorbent when all available adsorption sites are occupied and affinity of binding sites (L/mg), K_F and n are Freundlich constants, relevant to adsorption capacity and adsorption intensity, respectively.

The Langmuir and Freundlich constants were determined by linear regression method, from linear plots of C_e/q_e versus C_e and $\ln q_e$ versus $\ln C_e$, respectively. The results are shown in Table 1. It is clear that,both isotherm models represented well the experimental data, with R^2 values were higher than 0.9.However, Langmuir modelprovided a better fit with isotherm data of ILO than Freundlich model. This indicated that the sorption of PO_4^{3-} by ILO was probably monolayerand the surface of

ILO could be homogenous. On the other hand, Freundlich model was more efficient than Langmuir model in describing isotherm data for the sorption of PO_4^{3-} anions on both IZLO and ZLO. This finding revealed that the surface of IZLO and ZLO might beheterogeneous. In addition, there was a possibility of formation of multi layers on their surface during adsorption processes. In all cases, it was found that $n > 1$, implying the biosorption of PO_4^{3-} by ILO, IZLO, ZLO was favorable (de Lima et al, 2012).

Table 1

By comparing the maximum adsorption capacity of PO_4^{3-} anions, ZLO (47.88 mg/g) was found to be superior to IZLO (40.86 mg/g) and ILO (16.39 mg/g). Table 2 summarizes the maximum adsorption capacity of various biosorbents for the comparison purpose. It was found that IZLO and ZLO exhibited remarkable affinities towards PO_4^{3-}, which are favorably comparable with the majority of biosorbents reported in literature. Comparing with natural okara (2.45 mg PO_4/g), the phosphorus sorption capacities of ZLO and IZLO were boosted nearly 95%. The results proved that metal loading was an efficient method in enhancing the PO_4^{3-} sequestering ability of original okara. Biswas et al. (2008, 2007) claimed that, the adsorption of phosphate by metal loaded AWBs based biosorbents were possibly due to the ligand exchange mechanism, which occurred between PO_4^{3-} ions in the solution and OH^- ions coordinated with the metal ions loaded on AWBs based biosorbents. They suggested that, loaded metal ions could be easily converted into hydrated forms e.g. $[Ln(H_2O)_n]^{3+}$, $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, and $[Zr_8(OH)_{20}(H_2O)_{24}]^{12+}$ species, with the abundant amounts of OH^- ions and H_2O molecules. During the hydrolysis, H_2O molecules were deprotonated by releasing H^+ ions to form exchangeable OH^- ions, which could be replaced by PO_4^{3-} ions via ligand exchange mechanism. As can be seen from Table 2, q_m values of diverse biosorbents were reported at the operating conditions, which were different from thoseused for this study. Specifically, larger initial PO_4^{3-}concentration range was used by De Lima et al. (2012), lower pH values were used by Eberhardt et al. (2006), Krishnan and Haridas (2008), Mallampati and Valiyaveettil (2013), and higher dose of biosorbents was found in a research by Han et al.(2005). These results suggested that q_m values of three kinds of metal loaded okara in this study could be further improvedby optimizing the adsorption conditions.This wasstrongly supported by Fig.3, which displayed that the curves of IZLO and ZLO did not reach a constantin the investigated range of phosphorus concentration.Thus, for better comparison of the sorption capacity among biosorbents, q_m values at the optimum adsorption conditions should be determined and applied.

Table 2

Figure 3

3.2. Desorption of phosphorus and biosorbents reusability

Desorption of phosphorus paves the way to the recovery of this non–renewable resource, while reuse of a biosorbent gives a chance to reduce the cost of water treatment and to mitigate adverse impacts on the environment. For those reasons, desorbability and reusability of a biosorbent are very important to its applicability and need to be investigated in detail.Five solutions of 0.2 M NaOH, 0.05 M NaOH, pH 12 distilled water, 0.1 M HCl, and 0.1 M NaCl were evaluated for the elution of phosphorus from ZLO. The extremely low desorption percentage (<1%) for phosphoruswas found with both 0.1 M HCl and 0.1 M NaCl solutions. Higher desorption efficiencies were achieved with pH 12 distilled water (49.45%) and 0.05 M NaOH (70.76%). Among various eluants employed, 0.2 M NaOH was found to be most efficient, with the elution efficiency reached up to 97.8%. This can be explained by the replacement of PO_4^{3-} anions bound to the ZLO by OH^- ions during desorption process.

Also, the desorption results revealed that ion exchange might be an important mechanism in the adsorption of PO_4^{3-} by ZLO.This finding was in consistent with a previous study conducted by Unnithan et al. (2001), reporting that desorption efficiency of 96.8% could be achieved with 0.1 M NaOH.

Figure 4

Due to the satisfactory desorption result, 0.2 M NaOH was employed as a potential eluent in the following regeneration study with ZLO and IZLO. Fig. 4 displays the results of five continuous adsorption–desorption cycles obtained with ZLO and IZLO, which wereactivated by 0.1 M HCl after desorption with 0.2 M NaOH. Surprisingly,the phosphorus removal efficiency of both ZLO and IZLO dropped dramatically in the second cycle and stayed almost the same in the next cycles.After five cycles, the phosphorus removal efficiency reduced by 46.74%, while the phosphorus desorption efficiency decreased by 68.30% for ZLO. The corresponding values for IZLO were 42.93% and 64.83%. The desorption efficiency of ZLO and IZLO in the fifth cycle was just around 25%, which was too low for any application. pH values of solutions after adsorption from the second cycle on were found to be above 10. The results suggested that, the low phosphorus removal efficiency mentioned above was possibly due to high pH values, which hindered the capture of PO_4^{3-} anions. This assumption was tested by conducting other adsorption experiments with0.1 M HCl activated ZLO and IZLO. The results were depicted in Fig. 5.

Figure 5

After five cycles, the phosphorus removal efficiency of ZLO was reduced by 12.46%, whereas phosphorus desorption percentage only decreased by 7.40%. The corresponding values for IZLO were 21.91% and 17.45%. Evidently, activation of ZLO, IZLO with 100 mL of 0.1 M HCl resulted in more satisfying adsorption and desorption efficiencies. The pH values of the solutions after adsorption using 0.1 M HCl activated ZLO and IZLO were around 7.5. Comparing pH values and adsorption efficiencies obtained with ZLO, IZLO and those achieved with 0.1 M HCl activated IZLO, ZLO confirmed the hypothesis that, using 0.2 M NaOH for elution led to an increase in the pH values of adsorption solutions in the next cycle. Due to the unfavorable pH medium, the uptake of PO_4^{3-} in the next cycle was sharply declined. It would therefore appear that, 0.2 M NaOH is appropriate for long–term desorption of phosphorus from ZLO and IZLO if the desorbed biosorbents are activated with 0.1 M HCl before next adsorption cycle. The phosphorus adsorption and desorption efficiencies of ZLO remained about 85% after five consecutive adsorption–desorption cycles. This indicates the high reusability of ZLO for phosphorus decontamination. Significant decline in the adsorption and desorption efficiencies of IZLO (21.91% and 17.45%) after five continuous operation cycles might prevent this biosorbent from being reused.

3.3. Metal deposition on okara and metal release into aqueous solutions during adsorption and desorption tests

The PO_4^{3-} retention ability of a biosorbent is largely depends on the existence of loading metals on its surface (Carvalho et al., 2011). Thus, the loaded metal content exhibits not only the affinity of okara toward the metal, but also the PO_4^{3-} sorption capacity of that metal loaded okara. Table 3 represents data on metal deposition on okara and metal release into aqueous solutions during the performance of metal loaded okara. Table 3 shows that, 1 gram of natural okara was saturated with 21.62 mg of Fe(III)but 40.44 mg of Zr(IV), indicating the higher affinity of phosphorus toward Zr(IV) as compared to Fe(III).Based on the ratio of absorbed phosphorus to loaded metal, Zr(IV) was found to have a higher affinity toward PO_4^{3-} than Fe(III).The amount of Fe(III) deposited on IZLO accounted for only 8.79% of that on ILO. This indicated that a significant amount of Fe(III) was leaked during the pretreatment of ILO with Zr(IV) to produce IZLO. Simultaneously, some Fe(III) ions on ILO was probably replaced by Zr(IV) ions in the loading solution. The presence of Fe(III) on IZLO resulted in a reduction of 6.70% the amount of Zr(IV) used for okara loading as compared to ZLO. However, it should also be noted that the phosphorus uptake capacity of IZLO was 14.72% lower than that of ZLO. The results indicate that loading okara with combined Fe(III)/Zr(IV) solutions was not superior to doing that with single Zr(IV) solution. Fe(III) accounted for only 4.79% of the total amount of metals loaded on okara. Also, the affinity of Fe(III) toward $PO_4^{3-}$was inferior to Zr(IV) as mentioned above. Evidently, Fe(III) played a less important role than Zr(IV) in the capture of PO_4^{3-} by IZLO, in term of both the quantity and the affinity.

Table 3

The leakage of metals deposited on okara is a critical indicator for the unstability of the metal loaded okara. Tables 3 indicates that when ZLO was used for phosphorus removal, the content of Zr(IV) in the samples after adsorption and desorption processes was not detected. This provides strong evidence that ZLO is a stable biosorbent. Similar observation was noticed for Zr(IV) in case of IZLO. The results were in harmony with those in earlier studies (Biswas et al., 2008; Mallampati and Valiyaveettil, 2013), reporting that Zr(IV) could hardly be detached during its performance. On the other hand, in case of IZLO and ILO, the release of Fe(III) during adsorption process was significant, with 0.54 mg/g from IZLO and 1.59 mg/g from ILO. The latter value was in the same order of magnitude, when compared with 1.65 mg/g previously reported for wood particle treated with carboxymethyl cellulose and ferrous chloride (Eberhardt and Min, 2008). Taking into account the obtained results, it could be concluded that ZLO had the highest stability, followed by IZLO and ILO.

The metal leakage may cause adverse impacts on the aquatic medium if metals are toxic and their concentrations exceed the permissible levels.For$ZrOCl_2$, the fish toxicity (LC50) was found to be 15-270 mg Zr/L (*bluegill, fathead minnow*, 96 h) (Morning Star Consulting, Inc., 2005). In case of $FeCl_3$, the fish toxicity (LC50) was 92.8mg/L (*brachydaniorerio*, 48h), 75.6mg/L (*gambusiaaffinis*, 96h), 117mg/L (*poeciliareticulata*, 48h), 23mg/L (*oryziaslatipes* 48h) (http://www.thamesriverchemical.com/safetysheets/Ferric%20Chloride40solution.pdf). In this study, the highest concentrations of Zr(IV) and Fe(III) in aqueous solutions were found to be 0 and 12 mg/L, respectively. These values are far too low as compared to LC50 values mentioned above. This convinces that, the use of ILO, IZLO, ZLO as biosorbents of phosphorus cannot pose any risk to aquatic creatures.

3.4. Selection of the most suitable biosorbent for further investigation

ZLO offeredthe highest adsorption capacity (47.88 mg/g), which was equal or even better than several biosorbents reported in literature. Due to the high stability, ZLO can be used repeatedly without the necessity of metal reloading. Furthermore, the experimental data showed that ZLO could be recycled at leastfivetimes without a significant reduction in the phosphorus removal efficiency. Thus, ZLO can be a cost-effective biosorbent. Moreover,ZLO did not cause any harmful effects on the aquatic medium. Conversely, the use of IZLO and ILO for biosorption of phosphorus suffered from trivial limitations, such as notable metal leakage, fast drop in phosphorus removal efficiency after several cycles.Apparently, among three biosorbents investigated in this study, ZLO was the best choice for the elimination of phosphorus from aqueous solutions.

The applicability of ZLO not only depends on the adsorption capacity, desorption ability and reusability, but also the physical characteristics of the material. Thus, the present study examined such physical properties as density, porosity and permeability of ZLO. It was found that, ZLO (particle size range of 400-650 µm) has the bulk density of 0.36 g/cm^3, porosity of 50%, and permeability coefficient of 0.0079 m/s. Due to the low density and high porosity, ZLO is appropriate for being applied in up-flow column mode experiments. The initial investigation indicated that, ZLO can also be used in down-flow column mode experiments. These features should enhance the practical application of ZLO.

In the real wastewater, many anions may exist and thus competing with phosphate for anion binding sites on the adsorbents. Therefore, to evaluate the practical applicability of ZLO, the current study examined the phosphate removal of ZLO from synthetic wastewater, in the addition of individual or collective foreign anions. It was revealed that, addition of 10 fold higher molar concentrations of carbonate largely reduced the phosphate retention (23.52%), whilst sulfate, nitrate, chloride hardly interfered with the phosphate decontamination. The competing effect of carbonate can be ascribed to the higher affinity between ZLO and carbonate, when compared to that between ZLO and phosphate. However, this effect can be eliminated by conversion of dissolved carbonate salts into precipitated carbonate salts or gas carbon dioxide prior to the phosphate adsorption. The minimum interference of sulfate, nitrate and chloride can also be detected in the work conducted by Biswas et al. (2008, 2007), Jyothi et al. (2012). The results specify the potential of employing ZLO for the treatment of phosphate in the real wastewater.

4. Conclusion

ZLO proved to be superior to IZLO and ILO, with respect to adsorption, desorption and reusability. ZLO exhibited a relatively high phosphate adsorption capacity. Successful phosphate elution from spent ZLO was achieved with 0.2 M NaOH. By activation with 0.1 M HCl, ZLO could work proficiently for at least five consecutive cycles. The presence of common anions (i.g. sulfate, nitrate and chloride) hardly interfered with the performance of ZLO. The physical properties of ZLO favored its application in the column mode. Conclusively, ZLO can be used as a promising biosorbent for the treatment of phosphorus from aqueous solutions.

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FIGURE CAPTIONS

Fig. 1. Experimental set-up diagram

Fig. 2. Experimental design to determine the permeability coefficient of ZLO

Fig. 3. Isotherm of phosphorus adsorption by ILO, IZLO, ZLO (T = 298 K, t = 24 h, shaking speed = 120 rpm, C_i = 50mg/L, dose = 10 g/L, pH 7−7.5).

Fig. 4. The phosphorus adsorption and desorption efficiency obtained with ZLO and IZLO in 5 consecutive cycles (T = 298 K, t = 24 h, shaking speed = 120 rpm, C_i = 50 mg/L, dose = 10 g/L, pH 7−7.5).

Fig. 5. The phosphorus adsorption and desorption efficiency obtained with 0.1 M HCl activated ZLO and IZLO in 5 consecutive cycles (T = 298 K, t = 24 h, shaking speed = 120 rpm, C_i = 50 mg/L, dose = 10 g/L, pH 7−7.5).

FIGURES

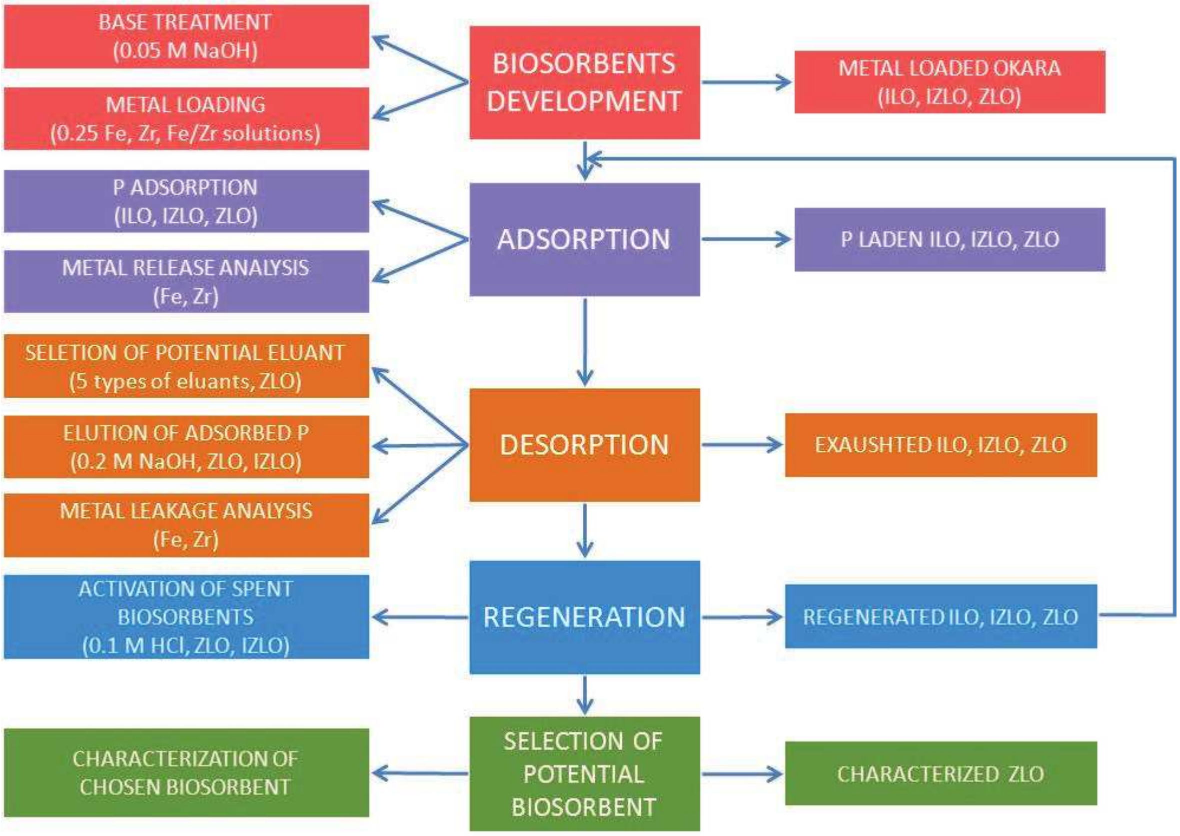

Figure 1

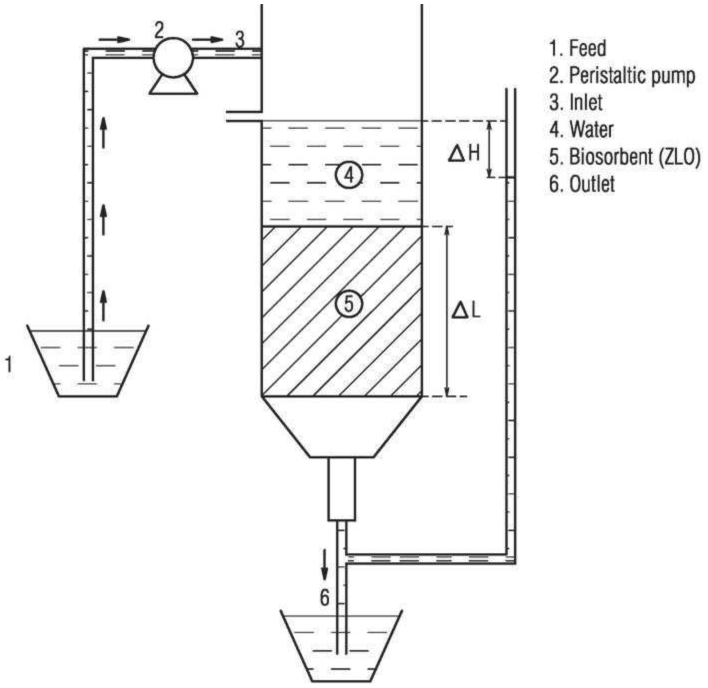
1
2
3
④
⑤
6
ΔH
ΔL
1. Feed
2. Peristaltic pump
3. Inlet
4. Water
5. Biosorbent (ZLO)
6. Outlet

Figure 2

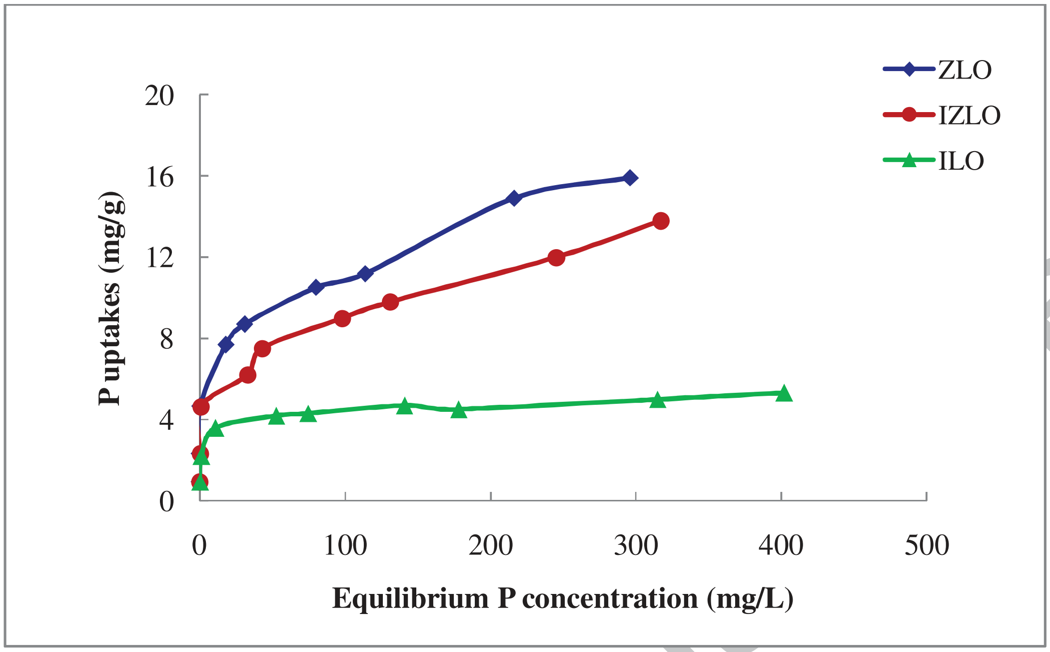
ZLO
IZLO
ILO
P uptakes (mg/g)
0
4
8
12
16
20
0
100
200
300
400
500
Equilibrium P concentration (mg/L)

Figure 3

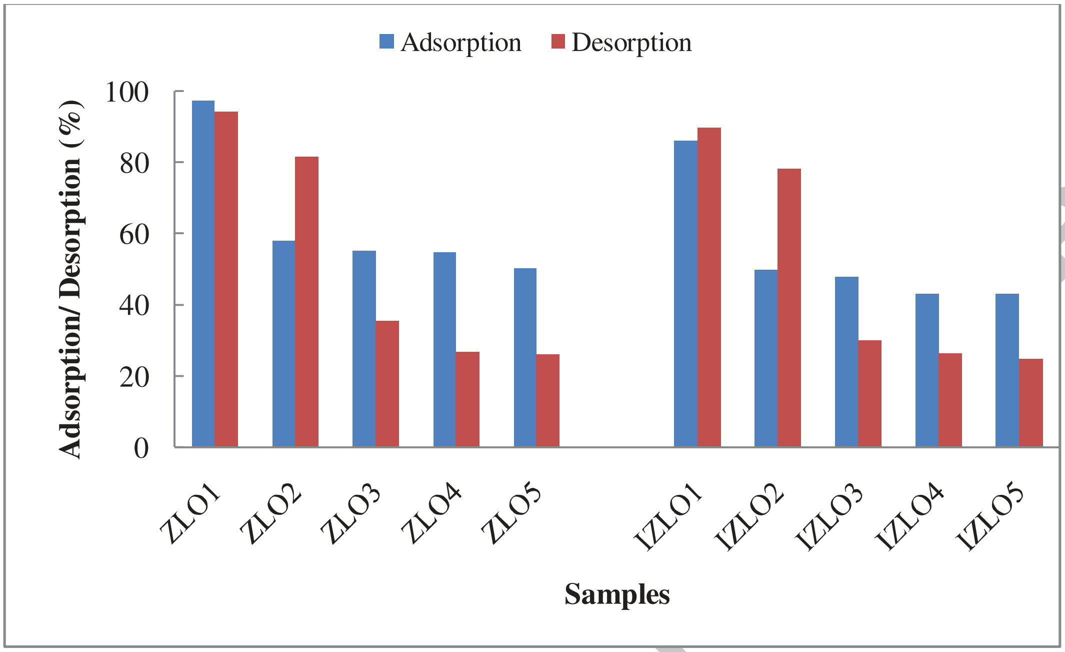
🟦 Adsorption
🟥 Desorption
Adsorption/ Desorption (%)
100
80
60
40
20
0
ZLO1
ZLO2
ZLO3
ZLO4
ZLO5
IZLO1
IZLO2
IZLO3
IZLO4
IZLO5
Samples

Figure 4

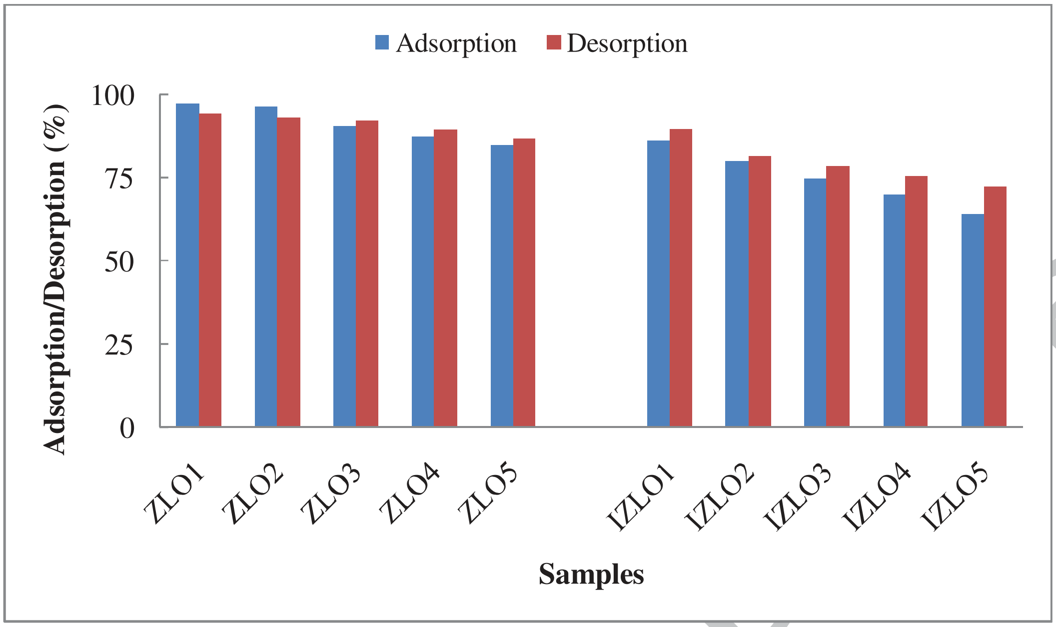
Adsorption
Desorption
Adsorption/Desorption (%)
100
75
50
25
0
ZLO1
ZLO2
ZLO3
ZLO4
ZLO5
IZLO1
IZLO2
IZLO3
IZLO4
IZLO5
Samples

Figure 5

TABLES

Table 1

Langmuir and Freundlich parameters for adsorption of PO_4^{3-}on ILO, IZLO, ZLO

Biosorbents	Langmuir constants			Freudlich constants		
	q_m (mg PO_4/g)	K_L (L/mg)	R^2	K_F mg/g(L/mg)$^{1/n}$	n	R^2
ILO	16.39	0.11	0.99	5.18	4.74	0.92
IZLO	40.86	0.04	0.96	11.48	4.98	0.97
ZLO	47.88	0.06	0.97	11.56	4.02	0.97

Table2

Comparison of ILO, IZLO, ZLO and various biosorbents reported in the literature, in term of the maximum PO_4^{3-} adsorption capacity.

Biosorbents	PO_4^{3-} concentration range (mg/L)	pH	Biosorbent dose (g/L)	Maximum adsorption capacity (mg PO_4/g)	Reference
Carboxymethyl cellulose/ Fe(II) treated aspen wood fiber	–	4.8	2	4.3	Eberhardt et al., 2006
Zn(II)activated coir pith carbon	10–40	3–10	6	5.10	Namasivayam and Sangeetha, 2004
Acid mine drainage treated juniper fiber	30.64	6.4	2–20	7.08	Han et al., 2005
Iron hydroxide eggshell	7–140	7.0	7.5	14.49	Mezenner and Bensmaili, 2009
Fe(III) loaded okara	***10–500***	***7.60–7.8***	***10***	***16.39***	***Present study***
Wood modified by carboxymethyl cellulose/ $FeCl_2$	0–100		4	17.38	Eberhardt and Min, 2008
Zr(IV) loaded apple peels	5–200	2–6	10	20.35	Mallampati and Valiyaveettil, 2013
Al(III) loaded skin plit waste	47.5–285	7.0	1	21.65	Huang et al., 2009
Cationized wood	–	3.0–9.0	–	25.65	Karthikeyan et al., 2004
Fe(III) loaded carboxylated polyacrylamide – grafted sawdust	9.50–23.75	2.5	2	28.79	Unnithan et al., 2001
Fe(III)/Zr(IV) loaded okara	***10–500***	***7.6–7.8***	***10***	***40.86***	***Present study***
Cationized bark	–	3.0–9.0	–	44.65	Karthikeyan et al., 2004
Zr(IV) loaded okara	***10–500***	***7.6–7.8***	***10***	***47.88***	***Present study***
Fe(III) loaded skin split waste	47.5–285	7.0	1	72	Huang et al., 2009
Fe(III) impregnated coir pith	20–200	3.0	2	70.92	Krishnan and Haridas, 2008
Bagasse fibrecarboxymethylated on surface and doped with $FeCl_2$ ions	2–10	–	–	152	Carvalho et al., 2011
Zr(IV) loaded orange waste gels		7.0	1.67	175	Biswas et al., 2008
Coconut shell fibers	20–1000		10	200	De Lima et al., 2012

Table 3

Deposition of metals on okara and their release into aqueous solutions during adsorption and desorption tests*

Biosorbents	Metal ions	Metal deposited on okara (mg/g)	Metal released during adsorption (mg/g)	Percentage of metal released during adsorption (%)	Metal released during desorption (mg/g)	Percentage of metal release during desorption (%)	P uptake capacity (mg/g)	P: metal ratio**
ILO	Fe(III)	21.62	1.59	7.35	3.30	15.26	5.35	0.25
IZLO	Fe(III)	1.90	0.54	28.42	0	0	13.33	0.34
	Zr(IV)	37.73	0	0	0	0		
ZLO	Zr(IV)	40.44	0	0	0	0	15.63	0.39

* The values for metal release during adsorption or desorption was the sum up of 3 continuous cycles.

** Ratio of P uptake capacity values to values for metal deposited on okara.

Highlights

- ZLO was superior to IZLO and ILO, especially in terms of affinity and reusability.
- ZLO could remove 97% P at the initial concentration of 50 mg/L, dose of 10 g/L.
- 0.2 M NaOH was suitable for elution of P from ZLO with the efficiency of 94.25%.
- No Zr(IV) leakage was observed during adsorption and desorption tests using ZLO.
- Activation of desorbed ZLO with 0.1 M HCl was necessary for ZLO to be recycled.